PB84-144146

Ambient Concentrations of Polycyclic Organic Matter

Radian Corp., Austin, TX

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

31 Oct 83

U.S. Department of Commerce
National Technical Information Service
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TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-450/5-83-010a		PB84 144146

4. TITLE AND SUBTITLE	5. REPORT DATE
Ambient Concentrations of Polycyclic Organic Matter	October 1983
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
S. A. Smith	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Radian Corporation 8501 Mo-Pac Blvd. P. O. Box 9948 Austin, TX 78766	11. CONTRACT/GRANT NO. 68-02-3818 Work Assignment 7

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Pollutant Assessment Branch, SASD Office of Air Quality Planning and Standards U. S. Environmental Protection Agency Research Triangle Park, N.C. 27711	14. SPONSORING AGENCY CODE EPA

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report is released to partially satisfy the requirements of Section 122 of the Clean Air Act, as amended in 1977. This report surveys and summarizes existing published polycyclic organic matter (POM) ambient concentration data. It presents technical data used to support decision making on the need for listing POM under Section 108 (a)(1), Section 112 (b)(1)(A), or Section 111 (b)(1)(A) as required by Section 122 of the Clean Air Act. Information is provided on the general sampling and analysis techniques employed for collection of POM ambient data. Data for specific POM compounds and particulate polycyclic organic matter are also presented.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Polycyclic Organic Matter BaP Hazardous Air Pollutant Collection Methods Analytical Techniques Particulate Organic Matter Polycyclic Aromatic Hydrocarbons Air Pollution	Hazardous Air Pollution Polycyclic Organic Matter	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Unlimited	Unclassified	70
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA 450/5-83-010a

PB84-144146

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DCN 203-012-07-04

AMBIENT CONCENTRATIONS OF POLYCYCLIC ORGANIC MATTER

Final Technical Note

EPA Contract No. 68-02-3818
Work Assignment 7

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1.0 INTRODUCTION

The purpose of this technical note is to briefly summarize existing published polycyclic organic matter (POM) ambient concentration data. A review and analysis of POM source and ambient concentration data prepared for EPA by the Research Triangle Institute (RTI) in 1980 (EPA-600/7-80-044)* provided a base set of data for this report. Eight additional studies published in periodicals or presented at technical conferences subsequent to the publication of the RTI report furnish more recent data on POM concentrations in urban and rural areas of the United States, a coke oven area in Canada, and a large urban center in Japan. These studies update the information and largely substantiate conclusions presented in the RTI report.

As defined in the RTI report, POM is a generic term applied to a large group of fused-ring organic compounds. In general, POM refers to those organic compounds consisting of two or more fused aromatic rings. The rings may either be comprised totally of carbon atoms or may contain hetero atoms of nitrogen, oxygen, and sulfur, in addition to other ring substitutes. Due to the large possible number of ring combinations and substitute permutations, the theoretical number of POM compounds can run into the millions; however, only approximately 100 have been identified in a single ambient air sample.*

There is no one accepted technique to analyze for POM content in air pollution samples. Many researchers analyze for specific POM compounds, which probably underestimates total POM concentrations. A few researchers analyze for the total organic fraction of captured particulate matter, which probably overestimates total POM concentrations.

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*White, J. B. and R. R. Vanderslice. (Research Triangle Institute). POM Source and Ambient Concentration Data: Review and Analysis. Prepared for U. S. Environmental Protection Agency. EPA-600/7-80-044. March 1980.

Although information is provided on the general sampling and analysis techniques employed for collection of POM ambient data, no attempt has been made to screen the data based on research methodology or to compare results of different studies. The data are presented as reported and demonstrate the range and variability of measured levels of POM occurring in the ambient air environment. No information is provided with respect to transformation/transport of POM in the atmosphere. The data are therefore useful only for preliminary evaluations of the potential public health consequences of exposure to POM in the ambient air.

Section 2.0 summarizes some general observations that can be made based on the data. POM ambient concentration data are presented in Section 3.0. Section 4.0 discusses the quality of the data and highlights sampling and analytical problems that influence the accuracy of estimates.

2.0 SUMMARY

A review of recent research on ambient concentrations of POM suggests the following observations:

1. Researchers use a diversity of techniques and procedures to analyze for POM content in air pollution samples. It is therefore misleading to make direct comparisons among the results of recent studies of POM ambient concentrations. No two researchers cited in this report have analyzed for the same array of individual POM compounds. Only two recent studies present data for total POM concentrations and these studies define POM as particulate organic matter, which includes more compounds than polycyclic organic matter. Other recent studies typically present the results of analyses for specific POM compounds, most often BaP and other polycyclic aromatic hydrocarbon (PAH) compounds. To further complicate a comparison of results, most studies analyzed for POM content in collected particulates; however, some studies attempted to collect both particulate and vapor-phase POM.

2. POM consists of two categories of compounds on the basis of the atomic constituents of the ring structures: polycyclic aromatic hydrocarbons (PAH) and heterocyclic polynuclear aromatics. The latter category, which includes aza arenes, oxa arenes, and thia arenes, is the least studied of the two. All of the studies cited in this report, except the two studies which defined POM as particulate organic matter, present results for concentrations of PAHs only.

3. Based on available data on BaP concentrations, normal background ambient air concentrations for POM in remote areas appear to be about 0.2 ng/m^3 or less.

4. POM concentrations in rural areas have been reported in different studies to range from 0.3 ng/m^3 (24-hr average) to 7,000 ng/m^3 (geometric mean for test period), reflecting the influence of POM transport from emission sources such as wood stoves, industrial plants, and urban centers.*

5. Urban atmospheric levels of POM have been reported in different studies to range from 2 ng/m^3 to 22,000 ng/m^3.* Ambient levels depend more on the type and concentration of emission sources than the size of the urban center.

6. Coke oven areas show consistently higher POM levels than non-coke oven areas. The ratio of POM concentrations in coke oven/non-coke oven areas ranges from 1.4 to 16.8.

7. Many studies have shown a pronounced seasonal variation in POM concentrations, with winter levels at some sites more than ten times higher than summer levels. However, other researchers dispute this finding, claiming that lower levels in summer are caused by increased volatilization and/or chemical degradation during sampling.

8. At least one researcher has reported significantly higher concentrations of nonpolar and moderately polar fractions of POM during daylight as compared to nighttime concentrations. No explanation was offered for the day-night variation.

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*The highest POM concentrations were reported in studies which defined POM as particulate organic matter rather than polycyclic organic matter.

9. POM exhibits preferential enrichment on smaller size particles, particularly in winter. Approximately 50 percent to more than 80 percent of the measured POM reportedly may reside on respirable particles ($\leq$ 3.5 μm).

10. Benzo(a)pyrene (BaP) is not a reliable indicator of total POM due to its reactivity in the atmosphere. Other problems with using BaP are variable BaP/POM ratios in ambient air and the trend of declining BaP emissions observed in recent years.

11. BaP ambient concentrations have been declining over the last 15 years due in part to controls on emissions from coke ovens, utilities, automobiles, and open burning. Ambient concentrations of POM compounds could increase in some areas, however, due to residential and industrial wood burning, combustion of refuse-derived fuel, vehicular traffic, and use of diesel fuel.

12. The accuracy of much ambient concentration data is uncertain due primarily to sampling and analytical problems. Sampling accuracy is influenced by the precision of the sampling apparatus, collection efficiency, potential filter losses, location of the sampling equipment, and frequency of sampling, extraction, and detection.

3.0 POM AMBIENT CONCENTRATION DATA

POM ambient concentration data are presented as reported in nine recent studies. The studies are:

1. White, J. B. and R. R. Vanderslice (Research Triangle Institute). POM Source and Ambient Concentration Data: Review and Analysis. Prepared for U. S. Environmental Protection Agency. EPA-600/7-80-044. March 1980.

2. Handa, T., Y. Kato, T. Yamamura, and T. I. Shii (Science University of Tokyo). "Correlation Between the Concentrations of Polynuclear Aromatic Hydrocarbons and Those of Particulates in an Urban Atmosphere." Environmental Science & Technology, Vol. 14, No. 4, April 1980. pp. 416-422.

3. Katz, M. and C. Chan (York University, Toronto, Ontario). "Comparative Distribution of Eight Polycyclic Aromatic Hydrocarbons in Airborne Particulates Collected by Conventional High-Volume Sampling and by Size Fractionation." Environmental Science & Technology, Vol. 14, No. 7, July 1980. pp. 838-843.

4. Hornig, J. F., R. H. Soderberg, D. L. Larsen (Dartmouth College) and C. Parravano (State University of New York, College at Purchase). "Ambient Air Assessment in a Rural New England Village Where Wood Is the Dominant Fuel." In: Proceedings: Conference on Wood Combustion Environmental Assessment, New Orleans, LA, February 21-24, 1981. Prepared by Research Triangle Institute for the U.S. Environmental Protection Agency. EPA 600/9-81-029 (PB81 248155). May 1981.

5. Greenberg, A. and F. B. Darack (New Jersey Institute of Technology). "Concentrations of Polycylic Aromatic Hydrocarbons at Four New Jersey Sites During An Extended Summer Sampling Campaign." Presented at the 75th Annual Meeting of the Air Pollution Control Association, New Orleans, LA, June 20-25, 1982.

6. Daisey, J. M., R. J. Hershman, and T. J. Kneip (New York University Medical Center). "Ambient Levels of Particulate Organic Matter in New York City in Winter and Summer." Atmospheric Environment, Vol. 16, No. 9, 1982. pp. 2161-2168.

7. Harkov, R. (New Jersey Department of Environmental Protection), J. M. Daisey and P. J. Lioy (New York University Medical Center). "Comparisons Between Summer and Winter Inhalable Particulate Matter, Fine Particulate Matter, Particulate Organic Matter, and SO_4 Levels at Urban and Rural Locations in New Jersey." Presented at the Air Pollution Control Association Specialty Conference on Measurement and Monitoring of Non-Criteria (Toxic) Contaminants in Air, Chicago, IL, March 22-24, 1983.

8. Manning, J. A., R. E. Imhoff (Tennessee Valley Authority) and G. G. Akland (U. S. Environmental Protection Agency). "Wintertime Ambient Measurements of Particulate Polycyclic Aromatic Hydrocarbons in a Residential Community." Presented at the Air Pollution Control Association Specialty Conference on Measurement and Monitoring of Non-Criteria (Toxic) Contaminants in Air, Chicago, IL, March 22-24, 1983.

9. Soderberg, R. H., J. F. Horning, A. Barefoot (Dartmouth College, and C. Parravano (State University of New York at Purchase). "Measurements of Polycyclic Aromatic Hydrocarbons in Ambient Air Particulates in Northern New England." Presented at the Air Pollution Control Association Specialty Conference on Measurement and Monitoring of Non-Criteria (Toxic) Contaminants in Air, Chicago, IL, March 22-24, 1983.

White and Vanderslice (the RTI report) provide a base set of data on POM ambient concentrations reported in studies published prior to 1978. The eight additional studies furnish updated information on measured levels of POM in the ambient atmosphere in areas of the United States, Canada, and Japan.

Two of these studies (Daisey, Hershman, and Kneip, 1982 and Harkov, Daisey, and Lioy, 1983) present data on total POM concentrations. However, these authors define POM as particulate organic matter rather than polycyclic organic matter. Their data, therefore, represent the organic fraction of particular matter, which includes organic compounds other than polycyclic organic matter. Although these data probably overestimate the concentration of polycyclic organic matter in ambient air, they can be viewed as an upper bound for ambient concentrations of POM.

The other six studies present the results of analyses for specific POM compounds, most often benzo(a)pyrene (BaP) and other PAHs. Table 3-1 identifies the POM compounds analyzed for and detected in each of these six studies. No two studies report the same array of individual POM compounds and no one study analyzed for more than 14 individual compounds. Furthermore, none of the studies present results for aza arenes, oxa arenes, or thia arenes, which comprise an important category of POM, the heterocyclic polynuclear aromatics. The results of these studies, therefore, probably underestimate the concentration of total POM in ambient air.

TABLE 3-1. SUMMARY OF POM COMPOUNDS DETECTED IN AIR POLLUTION SAMPLES IN SIX RECENT STUDIES

Compound	Handa et al., 1980	Katz and Chan, 1980	Hornig et al., 1981	Greenberg and Darack, 1982	Manning, Imhoff, and Akland, 1983	Soderberg et al., 1983
Anthanthrene		✓				
Anthracene			✓		✓	✓
Benz(a)anthracene	✓		✓	✓	✓	✓
Benzo(b)fluoranthene			✓	✓		
Benzo(j)fluoranthene				✓		
Benzo(k)fluoranthene		✓		✓	✓	
Benzofluoranthenes						✓
Benzo(r,s,t)pentapene		✓				
Benzo(g,h,i)perylene	✓	✓		✓	✓	✓
Benzo(a)pyrene	✓	✓	✓	✓	✓	✓
Benzo(e)pyrene		✓	✓	✓	✓	✓
Chrysene	✓		✓		✓	✓
Coronene				✓		✓
Cyclopenta(c,d)pyrene				✓		
Dibenz(a,c)anthracene				✓		
Dibenz(a,h)anthracene			✓	✓		
Dibenzanthracenes						✓
Dibenz(a,e)pyrene				✓		
Fluoranthene			✓		✓	✓
Indeno(1,2,3-c,d)pyrene				✓		✓
Naptho(1,2,3,d,e,f)chrysene		✓				
Perylene	✓	✓		✓		
Phenanthrene			✓		✓	✓
Pyrene	✓		✓		✓	✓
Triphenylene			✓		✓	

Section 3.1 summarizes general observations on measured levels of POM in the ambient air from these nine studies. Section 3.2 presents specific data and abbreviated excerpts from the reported research. Trends relating to ambient POM concentrations that are suggested by this recent research are discussed in Section 3.3. References used in addition to the nine studies primarily reviewed for this report are listed in Section 3.4. The studies listed above are referred to by author name and publication data in the discussion that follows.

3.1 Measured Levels - General Observations

3.1.1 Background Levels

Natural sources of POM, such as forest fires and volcanoes, can be considered to produce a natural background level of POM. Although it is impossible to separate the contributions of natural sources from those originating from the dispersal and long-range transport of POM from anthropogenic sources, measured levels in remote areas are indicative of background concentrations. The RTI report (White and Vanderslice, 1980) concludes that normal background ambient air concentrations for POM in remote areas appear to be about 0.2 ng/m^3 or less (based on BaP concentrations).

None of the other eight studies reviewed report data for remote areas, although several do report data for rural areas. Hornig, et al. (1981) reported levels totaling approximately 6 ng/m^3 for 12 POM compounds in two rural areas in New Hampshire (average of 48-hr data). Levels of from 0.3 ng/m^3 to 16.1 ng/m^3 of ten PAH compounds in rural Alabama are reported by Manning, Imhoff, and Akland (1983) (24-hr averages). Harkov, Daisey, and Lioy (1983) found levels as high as 4,400 ng/m^3 of POM (defined as particulate organic matter) in inhalable particulate matter in rural New Jersey in summer, and 7,000 ng/m in winter (geometric means for test period). Evidently, POM concentrations at rural sites can be heavily influenced by transport from potential POM emissions sources such as residences (wood stoves), industrial plants, and urban centers in the region.

3.1.2 Urban Concentrations

The RTI report concludes that urban atmospheric levels of POM may be 10 to 100 times higher than levels in remote areas, ranging from 2 to 20 ng/m^3. The highest concentrations are reported to be in coke oven areas. Much recent data indicate higher levels of POM in non-coke oven urban areas. Handa, et al. (1980) found 50 to 60 ng/m^3 of six PAH compounds in an urban area of the Tokyo Metropolitan Area (24-hr averages). Daisey, Hershman, and Kneip (1982) reported average levels of total POM (defined as particulate organic matter) on the order of 10,000 to 13,800 ng/m^3 in New York City, with levels reaching 22,000 ng/m^3 in the winter of 1977 when high sulfur fuel oil was burned during a fuel shortage in utility, commercial, and residential boilers. POM (defined as particulate organic matter) concentrations found by Harkov, Daisey, and Lioy (1983) in inhalable particulate matter at three urban areas in New Jersey corroborate the high levels reported in New York City.

3.1.3 Influence of Specific Sources

The RTI report presents data to demonstrate that POM levels (as measured by BaP) relate to the nature and degree of industrial and public activities, types and relative quantities of fuels consumed, degree of regulation exercised by authorities over emissions, volume of vehicular traffic, and extent to which photochemical and other reactions occur in the atmosphere. The chemical composition of POM will reflect combustion characteristics of each individual source or the dominance of a single type of source.

Areas near coke ovens tend to exhibit the highest reported levels of POM compounds. The U.S. Environmental Protection Agency conducted a comparative study of BaP concentrations in the air of cities with coke ovens over the period 1966-1972 (1). The coke oven cities were found to show consistently higher BaP levels in every year, with the ratios of coke oven/non-coke oven cities ranging from 1.42 to 3.34 and averaging about 2. The levels

of PAH found by Katz and Chan (1980) in a coke oven area in Canada (Hamilton Ontario) generally agree with EPA's findings. With the exception of anthanthrene, they report individual PAH concentrations from 1.8 to 16.8 times higher than corresponding PAH levels in New York City and Los Angeles (non-coke oven areas). Anthanthrene was slightly lower in Hamilton.

High automobile traffic density and high concentrations of wood burning sources also contribute to relatively higher ambient POM levels, particularly of specific compounds associated with these emissions sources. Coronene and benzo(g,h,i)perylene [B(ghi)P] have been shown to correlate with automobile traffic density better than other PAH (2). Greenberg and Darack (1982) found relatively high B(ghi)P/BaP ratios at urban New Jersey sites compared to a rural site. However, the coronene/BaP ratio was not consistently higher at the urban sites.

Hornig et al. (1981) suggest that high concentrations of benz(a) anthracene and chrysene identify wood smoke as a source of POM. However, they do not compare their data from wood burning areas in New Hampshire with other non-wood burning areas. These researchers are currently studying levoglucosan (1,6-anhydro-B-ϕ-glucopyranose) as a potentially useful qualitative and semiquantitative tracer for wood smoke.

3.1.4 Seasonal Variation

The RTI report presents data that show pronounced seasonal variation in POM concentrations, with winter levels of BaP at ten urban NASN sites more than ten times higher than summer levels. This effect is assumed to be a result of increased residential fuel combustion and local meteorology. However, in one study (3) discussed in the RTI report, the data indicate substantial seasonal variations in BaP in a coking region of Belgium even though there was no apparent change in the production of the source. In a subsequent series of wintertime experiments with filters heated from -2°C to 28°C, the authors were able to duplicate the seasonal trend in BaP. They concluded that

the seasonal trends in BaP concentrations detected in the coking region of Belgium were probably due to volatilization and/or chemical reactions on the filter surface that were catalyzed by trace elements. The authors did not discuss the possible effects of local meteorology on the observed seasonal variation.

Katz and Chan (1980) also present data from winter and summer sampling in a coke-oven area that show pronounced seasonal variation. (Winter levels were generally higher.) They used a cascade impactor with a low flow rate to minimize losses of PAH that may occur by sublimation from the deposit of particulate matter. The authors do not offer any explanation for the variation.

Daisey, Hershman, and Kneip (1982) report that atmospheric concentrations of total POM (defined as particulate organic matter) in New York City averaged 13,000 ng/m^3 for two summer periods and 16,000 ng/m^3 for two winter periods. After adjusting the data to account for dispersion, the authors conclude that POM emissions are three to four times higher in wint than in summer, primarily due to fuel combustion for space heating. Data reported by Harkov, Daisey, and Lioy (1983) for urban sites in New Jersey agree fairly well with this New York City data with respect to seasonal variation.

Data presented by Handa et al. (1980) for an urban area in the Tokyo Metropolitan Area, however, do not show a pronounced seasonal variation. They used a collection system with traps cooled by liquid nitrogen to collect the volatilized fraction of PAH.

3.1.5 Diurnal Variation

Daisey, Hershman, and Kneip (1982) investigated day-night differences in ambient concentrations of POM (defined as particulate organic matter) in New York City. They reported that nonpolar (cyclohexane-soluble) and

moderately polar (dichloromethane-soluble) fractions were found in significantly higher concentrations during daylight, while the polar (acetone-soluble) fraction showed no difference between day and night. The authors offer no explanation for the observed day-night variation.

3.1.6 Particle Size Distribution

Most of the studies cited in this report analyzed for POM content in collected particulates. Several researchers have noted the preferential enrichment of POM on smaller diameter particulates. This phenomenon is likely the result of the greater surface-to-volume ratios of small particles. Tests using particulate sizing techniques on urban aerosols have demonstrated that as much as 75 percent of the total BaP adsorbed onto particulate matter can reside on particulates with diameters less than 2.3 μm (4,5,6,7). Katz and Chan (1980) report that from 72.1 to 88.8 percent of individual PAH compounds measured for this study resided in the particle size range less than 3.3 μm. Data presented by Daisey, Hershman, and Kneip (1982) suggest a shift in the distribution of POM (defined as particulate organic matter) toward smaller size particles in winter. The authors report that respirable particles ($\leq$ 3.5 μm) contained a greater percentage of total POM in winter (81%) than in summer (54%).

3.1.7 BaP as an Indicator for POM

The RTI report concludes that neither long- nor short-term studies using benzo(a)pyrene as an indicator of total POM are reliable for quantitative ambient air quality estimates. Underestimation of total POM results from the failure to consider the apparent rapid decomposition rate of BaP, as well as the variable BaP/POM ratios in ambient air. Katz and Chan (1980) point out that BaP is an especially poor index of airborne POM in cities where motor vehicle traffic is one of the major sources of air pollution. In these areas, benzo(g,h,i)perylene is usually the dominant POM. In addition there has been an apparent decline in BaP concentrations in ambient air

over the last 15 years primarily resulting from controls on open burning and coke ovens (8). For these reasons, researchers now usually analyze ambient air samples for a variety of organic components.

3.2 Presentation of Specific Data

3.2.1 White and Vanderslice, 1980 (The RTI Report)

The RTI report reviews and analyzes POM ambient concentration data from more than 35 literature sources published between 1954 and 1977. The data are international in scope. The report cautions that ambient POM estimates, particularly those based on particulate sampling, contain a high degree of uncertainty due to sampling inaccuracies and chemical degradation of POM on the filter surface. Since the accuracy of the data base is not known, the report recommends that the data be considered semiquantitative, with measured POM concentrations best categorized as high, medium, or low.

The report draws four general conclusions from the ambient concentration data:

1. Normal background ambient air concentrations for POM in remote areas appear to be ≤ 0.2 nanograms/m^3. This conclusion is based on annual ambient BaP concentrations at three NASN remote stations, which averaged 0.1 nanograms/m^3 in 1976 (see Table 3-2). Urban atmospheric levels of POM may be 10 to 100 times higher.

2. Atmospheric POM concentrations as indicated by ambient BaP levels appear to be declining and are considered significantly less than the levels recorded 10 years ago. The data in Table 3-2 also demonstrate this trend.

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TABLE 3-2. ANNUAL AMBIENT BaP CONCENTRATIONS AT NASN STATIONS (ng/m^3)

Location	1966[a]	1970[a]	1976[b]	1977[b]
Honolulu	-	-	0.02	0.05
Chicago	-	-	0.53[c]	0.21[c]
Montgomery	-	-	0.26	0.04[c]
New Orleans	-	-	0.24	0.18
Baltimore	-	-	0.51	0.32
Detroit	-	-	1.1	0.42[c]
New York	-	-	1.0	0.47[c]
Youngstown	-	-	1.4	1.2
Bethlehem	-	-	0.33	0.15
Philadelphia	-	-	0.98	0.45
Chattanooga	-	-	0.27	0.66
Average for NASN Urban Stations	4.6	2.2	0.5[a]	0.28[b]
Average for 3 NASN Remote Stations	0.5	0.2	0.1[a]	-

[a]Reference 9

[b]Reference 10

[c]Based on three quarters reported

3. There is a pronounced seasonal variation in POM concentrations, which has been demonstrated in many areas. The data in Table 3-3 indicate that BaP levels in winter may be more than 10 times higher than in summer, although several sites in Canada exhibited slightly higher levels in summer.

4. The chemical composition of POM found in the atmosphere is a complex mixture reflecting combustion characteristics of each individual source or the dominance of a single type of source such as coke ovens of Birmingham, Alabama, or the vehicular traffic of Los Angeles, California (see Table 3-4). POM concentrations in coke oven areas are generally much higher than non-coke oven areas.

The RTI report contains a comprehensive compilation of data on POM concentrations in ambient air reported prior to 1978. The data are presented in three sets of bar graphs in an appendix: (1) BaP in urban air, (2) POM in urban air, and (3) POM in rural air. The authors made no effort to screen these data on the basis of the sampling and analysis techniques employed for collection.

3.2.2 Handa et al., 1980 (24-hr averages)

Handa et al. measured the atmospheric levels of six PAHs at several sites in the Tokyo metropolitan area, including three urban areas, two residential areas, two expressway tunnels and an underground cab pool. The ambient concentrations of benzo(g,h,i)perylene, benzo(a)pyrene, perylene, chrysene, benz(a)anthracene, and pyrene were initially based on the concentrations measured in samples collected with a high-volume air sampler. However, some of the PAH compounds containing four aromatic rings were not collected because it was not adsorbed on the particulate mass captured by the sampling apparatus. Therefore, the authors developed an improved collection system with traps cooled by liquid nitrogen. Sampling was subsequently conducted at Iidabashi, an urban area, during the winter of 1977 and the summer of 1978 using the improved cooling collection system (CCS-b) with a high flow rate.

TABLE 3-3. VARIATIONS IN SEASONAL AVERAGES OF BaP CONCENTRATIONS (ng/m^3)

Reference	Location	Year	Summer	Winter
11	Toronto	1972-73	12.6	17.1
9	Belfast	1962-63	9	51
9	Dublin	1962-63	3	23
9	Oslo	1962-63	36	103
9	Helsinki	1962-63	42	53
6	Canada--Average of 10 Towns	1971-72	0.50	0.71
		1972-73	1.2	0.85
6	Welland, Canada	1971-72	6.0	11.6
		1972-73	5.53	4.76
9	Urban USA--Average of 10 NASN Sites	1958-59	1.96	24.6

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TABLE 3-4. POM CONCENTRATION REFLECTING THE DOMINANCE OF A SINGLE SOURCE CATEGORY

	Site 1	Site 2	Site 3	Site 4	Average
POM Concentrations in Los Angeles Air (ng/m^3): Automotive Sources (1972)[a]					
Pyrene	2.0	1.4	3.8	0.16	1.8
Benz(a)anthracene	1.1	0.8	3.1	0.04	1.3
Benzo(e)pyrene	3.0	1.8	3.2	0.09	2.0
Benzo(a)pyrene	1.1	0.5	3.5	0.03	1.3
Fluoranthene	1.9	0.8	3.4	0.12	1.6
Benzo(g,h,i)perylene	9.2	4.2	7.1	0.21	5.2
Coronene	6.4	3.2	2.8	0.20	3.2
POM Concentrations in Birmingham, Alabama Air (ng/m^3): Coking Sources (1978)[b]					
Pyrene	4.6	10.8	9.1	2.5	6.8
Benz(a)anthracene	5.3	21.2	14.5	3.4	11.1
Benzo(e)pyrene	7.6	26.1	15.0	5.6	13.6
Benzo(a)pyrene	9.0	35.8	20.5	6.0	17.8
Fluoranthene	4.9	11.2	10.8	2.6	7.4
Benzo(g,h,i)perylene	9.5	22.4	15.3	7.9	13.8
Coronene	2.7	3.8	3.5	2.7	3.2

[a]Reference 2

[b]Reference 9

The results obtained at Iidabashi in the winter of 1977 are shown in Table 3-5. For comparison, simultaneous collection by an ordinary high volume air sampler was carried out at a location of 5 meters from the CCS-b apparatus. The atmospheric levels of all PAH compounds, determined from the sample captured on the first filter of the CCS-b, agreed well with those collected by the high-volume air sampler during the same period of time. The PAH captured in the second part of the CCS-b apparatus represents the fraction not ordinarily captured by a high volume air sampler.

Table 3-6 summarizes the data obtained at Iidabashi in the summer of 1978. A comparison of the results of this measurement with the results from the winter of 1977 does not show a pronounced seasonal variation as has been demonstrated in other studies (see Table 3-3). A larger fraction of PAH escaped the first filter of the CCS-b apparatus in summer than in winter, but significant amounts of missing PAHs were recovered in the cold traps and the back-up filter. The biggest differences are in the four-ring compounds pyrene, chrysene, and benz(a)anthracene.

3.2.3 Katz and Chan, 1980 (24-hr averages)

Katz and Chan collected airborne particulate samples by a conventional high-volume sampler and by an Anderson cascade impactor on 3 to 5 days in each month over a period of one year from June 1977 to May 1978 at two sampling sites in Hamilton, Ontario. Two sets of samples were collected over 24-hr periods at each site. Hamilton is the center of the largest concentration of iron and steel manufacturing facilities in Canada, containing the usual configurations of coke ovens, blast furnaces, and basic oxygen converters. Eight individual PAHs were separated and analyzed quantitatively by thin-layer chromatography and fluorescence spectrophotometry.

In general, markedly higher concentration levels of PAHs were found in samples collected at lower flow rates of about 0.57 m^3/min with the cascade impactor than with the high-volume air sampler (see Table 3-7). The authors conclude that the differences in amount of organic fraction are due

TABLE 3-5. DATA OBTAINED WITH CCS-b AND A HIGH-VOLUME AIR SAMPLER AT IIDABASHI IN WINTER 1977[a]

		Pyrene	Benz(a) anthracene	Chrysene	Perylene	Benzo(a) pyrene	Benzo(g,h,i) perylene
First Part	ng/m^3	11.8	4.3	5.4	0.6	2.4	8.1
	(%)	(35.1)	(66.2)	(68.4)	(85.7)	(85.7)	(95.3)
Second Part	ng/m^3	21.8	2.2	2.5	0.1	0.4	0.4
	(%)	(64.9)	(33.8)	(31.6)	(14.3)	(14.3)	(4.7)
Total	ng/m^3	33.6	6.5	7.9	0.7	2.8	8.5
H.V.A.S.	ng/m^3	14.7	4.4	4.5	0.7	2.0	7.8

[a]24-hr averages

TABLE 3-6. DATA OBTAINED WITH CCS-b AT IIDABASHI IN SUMMER 1978[a]

		Pyrene	Benz(a) anthracene	Chrysene	Perylene	Benzo(a) pyrene	Benzo(g,h,i) perylene
First Part	ng/m^3	7.3	4.1	4.0	0.7	2.4	5.8
	(%)	(28.7)	(52.6)	(59.7)	(77.8)	(82.8)	(92.1)
Second Part	ng/m^3	18.1	3.7	2.7	0.2	0.5	0.5
	(%)	(71.3)	(47.4)	(40.3)	(22.2)	(17.2)	(7.9)
Total	ng/m^3	25.4	7.8	6.7	0.9	2.9	6.3

[a]24-hr averages

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TABLE 3-7. COMPARISON OF AVERAGE CONCENTRATIONS OF PAH IN AIRBORNE PARTICULATES COLLECTED BY ANDERSEN CASCADE IMPACTOR VS. HIGH-VOLUME SAMPLER AT HAMILTON, ONTARIO, SAMPLING PERIOD, JANUARY-MAY, 1978[a]

	West-Central Site, ng/m^3		Barton-Wentworth Site, ng/m^3	
PAH	Andersen	High Volume	Andersen	High Volume
Benzo(a)pyrene	2.8	2.9	6.6	3.1
Benzo(e)pyrene	1.9	0.94	2.6	2.7
Perylene	0.35	0.12	0.56	0.31
Benzo(g,h,i) perylene	13.0	5.2	16.1	7.1
Benzo(k) fluoranthene	1.4	0.87	2.4	1.1
Naptho(1,2,3 d,e,f) chrysene	1.3	1.2	4.2	0.68
Anthanthrene	0.07	0.04	0.06	0.03
Benzo(r,s,t) pentapene	0.39	0.23	0.64	0.18

[a]24-hr averages.

to the volatilities of the PAHs and lower molecular weight compounds which can be lost through sublimation from the collected particulate matter in the presence of a higher air flow rate (about 1.5 m^3/min) through the filter of the high-volume sampler.

Comparative concentration levels of eight PAH compounds for the four seasons of the year are presented in Table 3-8. These data were reported to correspond with similar differences between warm and cold months of the year found in areas where principal sources of emissions are from the combustion of fossil fuels and motor vehicle traffic.

Katz and Chan also demonstrate the importance of size fractionation in the analysis of particulate samples of PAH. The average concentrations of eight PAHs in five size classifications from <1.1 to >7.1 μm and percentage distributions over the sampling period of one year are shown in Table 3-9. The particle size range of ≤1.1 to 3.3 μm contained from 72.1 to 88.8 percent of individual PAH compounds measured, while in the range of <1.1 to 7.0 μm, the percentages were as high as 87.5 to 95.1.

Katz and Chan compared annual average concentrations of PAHs in the air of Hamilton, New York City, and Los Angeles (see Table 3-10). With the exception of anthanthrene, the Hamilton PAH concentrations are considerably higher than corresponding PAH concentrations in the two much larger U.S. cities.

3.2.4 Hornig et al., 1981 (48-hr averages, but reported data is averaged over the test period)

During the 1979-80 heating season, Hornig et al. collected fifty standard hi-vol filter samples of ambient air in a small town (Lyme Center) in New Hampshire where wood is the dominant heating fuel. The town is free of industry and remote from a major highway. Three other sites were used for comparison: a residential area of Hanover, NH (pop. 6,000) and two sparsely settled rural sites (Moose Mountain and Brigham Hill) located several miles east and west of Hanover and close to several occupied residences.

TABLE 3-8. COMPARATIVE SEASONAL CONCENTRATION LEVELS OF PAHs IN AIRBORNE PARTICULATES, WEST-CENTRAL STATION IN HAMILTON, ONTARIO (CASCADE IMPACTOR SAMPLES)[a]

PAH	June-Aug, 1977 ng/m^3	Sept-Nov, 1977 ng/m^3	Dec-Feb, 1978 ng/m^3	March-May, 1978 ng/m^3
Benzo(a)pyrene	3.2	4.7	4.2	2.5
Benzo(e)pyrene	2.6	3.0	2.7	1.9
Benzo(k)fluoranthene	0.95	1.8	1.8	1.3
Perylene	0.30	0.60	0.44	0.35
Anthanthrene	0.12	0.19	0.11	0.07
Benzo(g,h,i)perylene	13.0	19.3	16.8	11.6
Naphtho(1,2,3 d,e,f)chrysene	2.2	2.2	2.4	1.2
Benzo(r,s,t)pentapene	0.65	0.60	0.47	0.26
Total PAH	23.1	32.5	28.9	19.1

[a]24-hr averages

TABLE 3-9. AVERAGE CONCENTRATIONS OF PAHs AND PERCENTAGES OF TOTAL IN PARTICULATE SIZE RANGES AT WEST-CENTRAL STATION IN HAMILTON, ONTARIO (ng/m^3)[a]

PAH	<1.1 μm		1.1-2.0 μm		2.0-3.3 μm		2.2-7.0 μm		>7.0 μm	
	Conc	%	Conc	%	Conc	%	Conc	%	Conc	%
Benzo(g,h,i)perylene	4.2	27.6	4.2	27.5	3.4	22.6	1.8	11.6	1.6	10.7
Benzo(a)pyrene	0.73	19.4	0.89	23.8	1.3	33.6	0.46	12.2	0.41	10.9
Benzo(e)pyrene	0.98	41.6	0.46	19.6	0.55	23.4	0.18	7.5	0.18	7.8
Naphtho(1,2,3 d,e,f)chrysene	0.91	46.7	0.48	24.8	0.34	17.3	0.11	5.8	0.11	5.5
Benzo(k)fluoranthene	0.63	43.5	0.27	18.9	0.32	22.1	0.13	8.9	0.10	6.6
Benzo(r,s,t)pentapene	0.12	29.3	0.10	25.6	0.07	17.0	0.06	15.5	0.05	12.5
Perylene	0.16	38.5	0.09	22.2	0.10	24.2	0.03	6.9	0.03	8.1
Anthanthrene	0.02	20.0	0.06	51.7	0.01	11.7	0.01	11.7	0.01	5.0

[a]24-hr averages

TABLE 3-10. ANNUAL AVERAGE PAH CONCENTRATIONS IN AIR OF HAMILTON, ONTARIO, NEW YORK CITY, AND LOS ANGELES (ng/m^3)

PAH	Hamilton			New York City[c] 1975	Los Angeles[d] 1974-1975
	West Central Site Cascade Impactor 1977-1978[a]	Barton-Wentworth Site High-Volume Sampler 1977-1978	Barton-Wentworth Site High-Volume Sampler 1975-1976[b]		
Benzo(a)pyrene	3.6	3.6	2.3	1.2-1.3	0.46
Benzo(e)pyrene	2.5	2.8	1.9	1.4	0.90
Benzo(k)fluoranthene	1.5	1.5	1.9	0.60	0.20
Perylene	0.42	0.30	0.29	0.10-0.20	0.10
Anthanthrene	0.12	0.02	0.18		0.23
Benzo(g,h,i)perylene	15.2	10.6	6.7	0.90	3.3
Naphtho(1,2,3 d,e,f)chrysene	2.0	0.89	1.0		
Benzo(r,s,t)pentapene	0.50	0.20	0.26		

[a] 24-hr averages

[b] Reference 11

[c] Reference 12

[d] Reference 13

Concentrations of 12 POMs in ambient particulate samples were determined using high pressure liquid chromatography (HPLC) with UV and fluorescence detection, and by GC/MS techniques. Numerical results, averaged over all filters collected at each site, are given in Table 3-11. Data are representative of 48-hr averages, averaged over the entire test period.

The authors draw several conclusions from these data:

1. The average POM concentrations in Lyme Center and the two rural sites are virtually identical, suggesting that on most days large-scale mixing of air, extending at least over the entire Connecticut River Valley area, dominates the Lyme Center environment.

2. The worst-case sample for Lyme Center shows that under appropriate conditions the local POM concentration can increase by a factor of more than five. Taking BaP as an index, the observed high value of 1.2 ng/m^3 approaches typical urban values, though it is still well below the values associated with areas near heavy coal-using facilities.

3. The overall POM burden in Hanover is comparable to the worst-case in Lyme Center.

The authors also compare their measurements to recently published BaP values from diverse sources (see Table 3-12). Values range from a low of 0.1 ng/m^3 in Coos County, NH to 208 ng/m^3 in the vicinity of coke ovens in Essen, Germany.

The authors express concern with several methodological problems with POM sampling and analysis techniques which potentially compromise much of the current ambient air POM data. In ongoing work, as interim measures, they plan to switch to Teflon-coated filters to minimize degradation on the

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TABLE 3-11. POM CONCENTRATIONS AT SEVERAL LOCATIONS IN NEW HAMPSHIRE IN THE WINTER OF 1979-1980 (ng/m^3)[a]

Substance	Lyme Center (Average)	Urban Hanover (Average)	Moose Mtn. New Hampshire (Average)	Brigham Hill Vermont (Average)	Worst Case Lyme Center
Phenanthrene	0.01	0.63	0.18	0.12	0
Anthracene	0.02	0.08	0.02	0.03	0.04
Fluoranthene	0.44	2.6	0.41	0.40	2.6
Pyrene	0.49	3.1	0.43	0.52	2.7
Triphenylene	0.04	0.52	0.17	0.15	0
Benz(a)anthracene	0.41	1.3	0.33	0.32	1.4
Chrysene	0.63	1.8	0.61	0.44	2.1
Benzo(e)pyrene	0.93	2.6	0.87	0.74	2.2
Benzo(b)fluoranthene	0.83	1.9	0.88	0.54	2.9
Benzo(a)pyrene	0.54	1.5	0.37	0.50	1.2
Dibenz(a,h)anthracene	1.9	4.8	1.7	1.3	6.7
Benzo(g,h,i)perylene	0.65	1.8	0.55	0.47	2.1
Total	6.9	20.3	6.5	5.5	23.9

[a]Average for heating season October-April.

TABLE 3-12. AMBIENT BaP CONCENTRATIONS IN VARIOUS LOCATIONS

Location	BaP Concentration (ng/m^3)	Conditions	Reference
New York City, NY	0.3-3.5	Aug. 1976	14
Pasadena, CA	0.39-1.06	Oct. 1976-Mar. 1977	15
Karlsruhe, Germany	0.2-42.5	Oct. 1975-Mar. 1976	16
New York City, NY	1.15-1.30	Annual average, 1975	12
Claremont, CA	0.17-1.16	Spring 1979	17
Toronto, Canada	0.1-0.8	Two summer and two winter months 1974	18
Essen, Germany	6-60	Residential coal heating area	19
	1.3-66	Oil heating area	
	2-100	Auto tunnel	
	11-208	Vicinity of coke ovens	
	0.5-8	Rural location	
Lake Michigan	0.3-1.8	Spring, summer, fall June 1975-Aug. 1977	20
Hamilton, Ontario (See Section 3.2.3)	2.3-3.6	Annual average for 1975/76 and 1977/78	21
Los Angeles, CA	0.46	Annual average, 1974/75	13
Chicago, IL	1.0	Annual average, 1975	22
New York City, NY	0.9	Annual average, 1975	22
Pittsburgh, PA	2.1	Annual average, 1975	22
Tucson, AZ	0.4	Annual average, 1970	22
Ashland, KY	4.7	Annual average, 1975	22
Anchorage, AK	0.8	Annual average, 1970	22
Denver, CO	2.2	Annual average, 1970	22
Duluth, MN	1.1	Annual average, 1970	22
Altoona, PA	19.3	Annual average, 1970	22
Youngstown, OH	7.1	Annual average, 1970	22
Coos County, NH	0.1	Annual average, 1970	22

filter and to sample extraction by sonification instead of Soxhlet extraction to reduce the time and severity of that step. They have adopted a solvent extraction technique to clean up the samples before analysis by HPLC or GC/MS. Sample handling will be conducted in a room equipped with yellow fluorescent light to minimize changes of photooxidation (see Section 3.2.9).

3.2.5 Greenberg and Darack, 1982

During the period of July 6 to August 14, 1981, Greenberg and Darack collected inhalable airborne particulate samples at four New Jersey sites: Newark, Elizabeth, Camden, and Ringwood. A high-volume sampler was used for sample collection. Cyclohexane extracts of daily samples (24-hr average) at the three urban sites and three-day composites for the rural site (Ringwood) were analyzed for PAH content.

Table 3-13 lists concentrations of PAH from six-week composites obtained in Newark, Elizabeth, and Camden. Duplicate analyses were run for the Newark composites. Duplicate samples were analyzed for the Elizabeth composite.

Table 3-14 lists the Newark, Elizabeth, and Camden six-week composite averages in addition to averages of the data for all four sites. The Newark averages are presented in two columns: (A) without the singularly high levels of BaP (8.74 ng/m^3) and other PAH found at the Newark location on July 21-22, 1981, and (E) including those high levels.

The authors draw the following conclusions from the data:

1. The average PAH concentrations at the three urban sites (Newark, Elizabeth, and Camden) are very similar and much higher than at the rural site (Ringwood). These concentrations are comparable to previously-obtained summer data (23).

TABLE 3-13. CONCENTRATIONS OF PAH OBTAINED FROM NEWARK, ELIZABETH AND CAMDEN - SUMMER (July 6 - August 14), 1981 COMPOSITES (ng/m^3)[a]

PAH	Newark Trial 1	Newark Trial 2	Elizabeth Trial 1	Elizabeth Trial 2	Camden Trial 1
Cyclopenta(c,d)pyrene	-	-	-	-	0.20
Benz(a)anthracene	-	0.18	-	0.07	0.11
Benzo(e)pyrene	0.33	0.34	0.13	0.13	0.13
Benzo(j)fluoranthene	0.32	0.33	1.12	0.13	0.16
Perylene	0.47	0.50	-	0.15	0.09
Benzo(b)fluoranthene	0.55	0.57	0.40	0.22	0.37
Dibenz(a,c)anthracene	0.03	0.06	0.01	0.01	0.01
Benzo(k)fluoranthene	0.37	0.30	-	0.11	0.14
Benzo(a)pyrene	0.42	0.45	0.19	0.18	0.22
Dibenz(a,h)anthracene	0.02	-	-	-	0.02
Benzo(g,h,i)perylene	0.73	0.86	0.64	0.59	0.45
Indeno(1,2,3-c,d)pyrene	1.1	1.1	0.54	0.43	-
Dibenz(a,e)pyrene	0.35	0.39	0.14	0.11	-
Coronene	0.68	0.76	-	0.36	-
Total	5.4	5.8	2.2	2.5	1.9

[a]Six-week composites of daily samples.

TABLE 3-14. AVERAGES OF DAILY PAH DATA AT FOUR NEW JERSEY LOCATIONS DURING SUMMER, 1981, AND COMPARISON WITH SIX-WEEK COMPOSITE DATA (ng/m^3)[a]

PAH	A Newark Average[b]	B Elizabeth Average	C Camden Average	D Ringwood Average[c]	E Newark Average[d]	Six-Week Composite Data		
						Newark[e]	Elizabeth	Camden
Cyclopenta(c,d) pyrene	0.21*	0.11*	0.46*	0.03*	0.44*	-	-	0.20
Benz(a) anthracene	0.22	0.13*	0.21	0.03*	-	0.16	0.07	0.11
Benzo(e) pyrene	0.23	0.20	0.21	0.04	0.39	0.29	0.13	0.17
Benzo(j) fluoranthene	0.19	0.14	0.17	0.06	0.36	0.33	0.13	0.16
Perylene	0.15	0.07	0.09	0.05*	0.27	0.41	0.15	0.21
Benzo(b) fluoranthene	0.33	0.29	0.32	0.08	0.70	0.56	0.31	0.36
Dibenz(a,c) anthracene	0.04	0.03	0.03	0.02*	0.06	0.04	0.01	0.01
Benzo(k) fluoranthene	0.24	0.18	0.18	0.04*	0.51	0.33	0.11	0.16
Benzo(a)pyrene	0.28	0.21	0.27	0.07	0.53	0.42	0.19	0.24
Dibenz(a,h)anthracene	0.02	0.04	0.02	0.01*	0.02	0.01	-	0.02
Benzo(g,h,i) perylene	0.63	0.54	0.46	0.10	0.87	0.75	0.62	0.57
Indeno(1,2,3-c,d) pyrene	0.77	0.60	0.61	0.15	1.3	1.1	0.49	0.62
Dibenz(a,e)pyrene	0.77	0.18*	0.83*	0.14*	-	0.37	0.12	0.24
Coronene	0.31	0.28	0.22	0.07*	-	0.71	0.36	0.51
Total	4.4	3.0	4.1	0.89	5.5	5.5	2.7	3.6

[a] Newark, Elizabeth, and Camden are urban sites. Ringwood is a rural site.

[b] Without 7/21-22/81 singularity.

[c] Ringwood data are averages of 3-day samples, other sites are averages of 24-hr samples.

[d] All data including 7/21-22/81 singularity.

[e] Composite includes 7/21-22/81 singularity.

* Denotes average value where the total number of measurements was less than 10.

2. A very high PAH level was found on July 21-22, 1981 at the Newark site possibly resulting from "a local combustion source" and a weather stagnation period. This single 24-hour period caused the Newark summer composite to have about twice the PAH concentration of either the Elizabeth or Camden composites.

3. The relative automobile exhaust contributions to PAH appeared to follow the site order: Elizabeth > Newark > Camden > Ringwood. This ranking is based on higher B(ghi)P/BaP and coronene/BaP ratios being indicative of the relative contribution of auto traffic.

3.2.6 Daisey, Hershman, and Kneip, 1982

Daisey et al. collected twenty-four hour hi-vol samples of total suspended particulate matter on fiberglass filters from noon to noon in New York City during periods of August 1976, February 1977 and January-February 1978. Twelve-hour samples were also collected from 0600 to 1800 hour and 1800 to 0600 hour during August 1977 to examine daytime vs. nighttime variations. Increasingly polar solvents (cyclohexane, dichloromethane, and acetone) were used to extract nonpolar, moderately polar, and polar organic fractions, respectively, from the samples. The sequential extracts were analyzed for total POM content. The authors define POM as particulate organic matter which includes organic compounds other than polycyclic organic matter.

Samples were collected at the New York University Medical Center Station, which is located on a roof (60 meters above the street) in midtown Manhattan. Long-term studies involving weekly samples collected at this same site are on-going.

Table 3-15 presents estimates of the fraction of particulate organic matter present in respirable particles for the August 1977 and January-February 1977 sampling periods. These data indicate that the respirable particles contained a greater fraction of the particulate organic matter in the winter sampling period (81%) than in the summer sampling period (54%). Atmospheric concentrations of total particulate organic matter averaged 13,000 ng/m^3 for the two summer periods and 16,000 ng/m^3 for the two winter periods, although the data for August 1977 and January-February 1978 in Table 3-15 do not exhibit this seasonal variation.

Data normalized to account for differences in dispersion show twice as much particulate organic matter for August 1976 as for August 1977. This may have been due to more rainfall during the 1977 period (washing particulates out of the atmosphere) or to differences in source emissions and atmospheric chemistry. Average dispersion normalized concentrations of particulate organic matter for the two winter sampling periods also indicate emissions in winter 1977 were twice as high as those in 1978. The authors suggest that the higher particulate organic matter concentrations observed in February 1977 are attributable in large part to the burning of high-sulfur fuel oil in utility, commercial, and residential boilers during a fuel shortage in the winter of 1976-1977. On average, dispersion-normalized concentrations of particulate organic matter for the winter sampling periods are three to four times higher than those of the summer.

The differences in dispersion-normalized estimates are useful for determining when particulate organic matter emissions are greatest. However, dispersion-normalized concentrations do not reflect the actual ambient concentrations to which the population is exposed. Dispersion in the New York City area is greater in winter than in summer.

In Table 3-16, the TSP and particulate organic matter data for 1977 and 1978 are compared to similar measurements made at the same site in 1968 and 1969. These data show sharp declines in particulate levels. However, airborne concentrations of particulate organic matter in the 1978 winter

TABLE 3-15. SEASONAL VARIATIONS IN RESPIRABLE AND NON-RESPIRABLE PARTICULATE ORGANIC MATTER IN NEW YORK CITY (ng/m^3)

	No. of Tests	Non-polar[d]	Moderately Polar[e]	Polar[f]	Total
August 1977					
RSP[a]	2	2,200	400	4,000	6,600
TSP[b]	31	4,100	900	7,100	12,100
RSP/TSP x 100%		54	44	56	54
January-February 1978					
RSP[a]	4	3,300	700	4,100	8,100
TSP[c]	24	4,000	600	5,400	10,000
RSP/TSP x 100%		83	117	76	81

[a]Average of weekly samples of RSP (≤3.5 μm aerodynamic diameter) covering the same sampling period as the TSP samples.

[b]Average of 12-h TSP samples.

[c]Average of 24-h TSP samples.

[d]Extracted with cyclohexane.

[e]Extracted with dichloromethane.

[f]Extracted with acetone.

RSP = Respirable suspended particulates.

TSP = Total suspended particulates.

TABLE 3-16. A COMPARISON OF 1976, 1977, AND 1978 MEASUREMENTS OF TSP AND PARTICULATE ORGANIC MATTER TO MEASUREMENTS FOR 1968 AND 1969 AT THE SAME SITE IN NEW YORK CITY (ng/m^3)[a]

	No. of Tests	TSP	POM[e]	Percent POM[e] in TSP
Winter				
Jan-Feb 1968[b]	9	143,000	11,300[c]	7.9
Jan-Feb 1969[b]	7	130,000	8,300[c]	6.4
Feb 1977	21	96,000	22,000[d]	22.9
Jan-Feb 1978	24	66,000	10,000[d]	15.2
Summer				
August 1968[b]	3	106,000	9,700[c]	9.2
August 1969[b]	4	84,000	7,700[c]	9.2
August 1976	17	115,000	13,800[d]	12.0
August 1977	31	116,000	12,100[d]	10.4

[a]Mean concentration.
[b]Weekly samples.
[c]Sum of concentrations of benzene- and acetone-soluble organics.
[d]Sum of concentrations of cyclohexane-, dichloromethane- and acetone-soluble organics.
[e]particulate organic matter

sampling period did not differ significantly from those in 1968 and 1969. (The higher concentrations of both TSP and particulate organic matter in winter 1977 appear to have been related to an exceptional period when variances were granted to burn high-sulfur fuel oil.) Although conversion to low-sulfur (and low-ash) fuel oil for winter space heating has reduced TSP through a reduction of mineral content, particulate organic matter emissions appear to have changed little based on a comparison of the January-February 1977 data in Table 3-16 with January-February data for 1968 and 1969. However, the data may not be directly comparable because more tests were conducted in the later study and different solvents were used to extract the organic content.

Concentrations of particulate organic matter during the summer sampling periods of 1976 and 1977 were about 40 percent higher than for similar periods in 1968 and 1969. The authors attribute this difference to "regional accumulation" and transport of airborne pollutants from regions to the west of the city during the summers of 1976 and 1977.

The authors conclude from the data that combustion of fuels for space heating in residences, apartment buildings, office buildings, and similar locations is currently the most important source of particulate organic matter in New York City and that changes in fuel oil composition can substantially increase ambient concentrations of particulate organic matter under certain conditions (e.g., winter of 1977 when the use of high sulfur oil increased).

3.2.7 Harkov, Daisey, and Lioy, 1983

The New Jersey Atmospheric Toxic Element and Organic Species (ATEOS) program is designed to measure the levels of inhalable particulate matter (IPM: $\leq$ 15 μm) and constituent species in the state. In the ATEOS program, the following constituents of IPM are quantified: fine particulate matter (FPM: $\leq$ 2.5 μm), SO_4^{-2}, extractable POM, PAH, and trace elements. POM

is defined as particulate organic matter rather than polycyclic organic matter. Levels of these constituents were measured for four sites in New Jersey during the 1981 summer (see Section 3.2.5) and 1982 winter monitoring campaigns.

Samples were collected using General Metal Works SSI ($\leq$ 15 μm) high-volume (40 cfm) samplers and Aerotech #2 cyclone ($\leq$ 2.5 μm) samplers (25 cfm). Samplers were run from 10:00 a.m., seven days/week for six weeks in the summer (7/6-8/13/81) and winter (1/18-2/25/82) at three urban (Newark, Elizabeth, Camden) and one rural site (Ringwood). The particulate organic matter was determined using a three-solvent (cyclohexane, dichloromethane, acetone) sequential Soxhlet extraction (see Section 3.2.6).

Table 3-17 shows the geometric means for selected constituents of IPM collected at the four sites. Concentrations of particulate organic matter show urban-rural and seasonal variations. Particulate organic matter levels at Ringwood are on average approximately half the levels found at the three urban sites. Summer concentrations at all sites are slightly more than half the winter concentrations. The particulate organic matter fraction constituted between 19 and 22 percent of the IPM mass in summer 1981 and between 29 and 37 percent of the IPM mass in winter 1982.

Peak values for particulate organic matter during summer and winter pollution episodes are shown in Table 3-18. Peak levels of particulate organic matter in summer increased by a factor of three during periods of high levels of IPM and constituted up to 31 percent of the IPM mass at urban sites. In winter, particulate organic matter levels reached peak values of up to 57 percent of the IPM mass during pollution episodes.

A special study of fine particle particulate organic matter levels at Elizabeth during the winter of 1982 campaign has not yet been published.

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TABLE 3-17. GEOMETRIC MEANS FOR SELECTED IPM CONSTITUENTS AT FOUR SITES IN NEW JERSEY (ng/m^3)

	N[b]	IPM[c]	FPM[d]	SO_4^{-2}	Cx[e]	DCM[f]	ACE[g]	POM[h]
Summer 1981								
Newark	39	46,300	25,600	10,400	3,200	900	6,300	10,400
Elizabeth	39	34,800	20,100	11,300	2,200	600	4,800	7,600
Camden	39	40,600	27,700	10,300	2,000	600	6,000	8,600
Ringwood[a]	39	23,300	9,700	10,700	800	400	3,200	4,400
Winter 1982								
Newark	39	47,300	36,900	10,700	5,400	1,500	10,500	17,400
Elizabeth	39	46,200	-	10,500	5,800	1,300	8,300	15,400
Camden	39	41,600	33,400	11,600	3,400	1,100	7,200	11,700
Ringwood[a]	39	24,500	23,600	9,500	1,500	900	4,600	7,000

[a] Ringwood data represents 3-day composites for SO_4 and POM measures, N = 12.

[b] Number of measurements

[c] Inhalable particulate matter

[d] Fine particulate matter

[e] Cyclohexane-soluble organics

[f] Dichloromethane-soluble organics

[g] Acetone-soluble organics

[h] Particulate organic matter

TABLE 3-18. PEAK LEVELS OF PARTICULATE ORGANIC MATTER IN NEW JERSEY DURING SUMMER AND WINTER POLLUTION EPISODES (ng/m^3)

	Camden	Newark	Elizabeth	Ringwood
Summer 1981				
7/19-20	13,900	28,900	20,200	6,900
8/4-5	10,500	19,900	9,600	3,000
8/9-10	12,200	10,800	9,700	5,400
8/10-11	11,300	26,000	16,600	5,900
Winter 1982				
1/19-20	14,800	24,700	22,700	8,000
1/28-29	25,400	34,500	40,300	11,200
1/29-30	29,500	37,200	31,500	11,200
2/5-6	18,400	27,800	34,300	9,100
2/11-12	29,800	22,500	22,700	12,200
2/15-16	18,400	31,200	29,500	13,800

3.2.8 Manning, Imhoff, and Akland, 1983

Total suspended particulates and the fraction of coarse and fine particles in the samples were measured in a residential community in a suburb of Florence, Alabama and at a nearby rural site from December 23, 1981 to March 22, 1982. Standard hi-volume samplers were used to collect TSP on fiberglass filters. About 70 of these samples were analyzed for BaP and other PAH. In this paper, "total" refers to particulate plus vapor phase PAH for a given species or combination of species.

The suburban site was located in a middle class subdivision with about 65-75 percent of the houses having either wood heaters or fireplaces. The rural site was located about 10 km away with no house within about 2.4 km but close to a school using coal as a fuel for heat.

Table 3-19 shows ambient TSP and BaP concentrations determined using thin layer chromatographic procedures. BaP concentrations ranged from below detectable limits to 7.24 ng/m^3. Since results for all days were not analyzed for BaP, a true seasonal average cannot be given. However, means for the residential and rural sites were 2.36 and 0.54 ng/m^3, respectively.

Table 3-20 shows recent limited BaP data available through the EPA particulate sampling network. These data indicate that for other southeastern cities, wintertime averages ranged from between 0.26 to 3.31 ng/m^3 in 1981 and 1982.

Many PAH compounds, including BaP, were identified for this study by PEDCo using standard GC/MS procedures. These data are presented in Table 3-21. The total for ten PAHs ranges from 0.56 to 73.2 ng/m^3 at the residential site and from 0.30 to 16.1 ng/m^3 at the rural site.

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TABLE 3-19. AMBIENT TSP AND BaP CONCENTRATIONS AT FLORENCE, ALABAMA, DECEMBER 23, 1981 - MARCH 22, 1982 (EPA TLC* METHOD)

Date	TSP ($\mu g/m^3$)	BaP (ng/m^3)
Residential		
12-25	49	3.33
1- 4	49	3.99
5	52	4.11
6	36	0.84
9	54	3.63
10	43	2.11
15	65	1.14
17	62	4.52 [0.80][a]
18	67	7.24 [6.49][a]
24	64	5.20
29	46	1.20
2- 7	27	2.56
9	20	0.47
10	23	0.52
11	39	1.10
12	36	1.54
13	71	7.08 (6.75)[5.39]
14	61	4.19
15	41	2.22
16	23	<0.35
20	51	2.74
3- 2	52	1.80
6	16	<0.34
16	26	<0.36
17	32	<0.35
18	35	<0.35
22	24	<0.36
Average	43 (±16)[b]	2.36 (±2.05)
Rural		
12-25	27	0.63
1- 4	22	<0.28
5	43	1.82
6	28	<0.27
10	66	0.67
24	10	<0.27
2- 9	20	0.27 (0.30)
10	16	<0.27 [0.36]
11	19	0.47
13	22	<0.27
15	29	1.12
16	19	0.42
23	45	0.98
24	39	<0.30
3-17	33	<0.30
21	17	<0.27 (<0.27)
Average	28 (±14)	0.54 (±0.43)

[a] [] Indicates PEDCo results; () indicates blind duplicate by EPA.
[b] Values in parentheses are standard deviations.
* TLC - Thin layer chromatography.

TABLE 3-20. FIRST AND FOURTH QUARTER BaP CONCENTRATIONS AT AVAILABLE SOUTHEASTERN SITES, 1981-1982 (ng/m^3)

Site	First Quarter		Fourth Quarter	
	1981	1982	1981	1982
Birmingham, AL	--	0.57(7)[a]	0.40(8)	--
Jefferson County, AL	--	1.35(8)	3.31(8)	--
Jacksonville, FL	0.56(6)	--	--	--
Baton Rouge, LA	0.28(5)	--	--	--
New Orleans, LA	0.26(7)	--	--	--
Chattanooga, TN	--	1.30(8)	1.99(7)	--

Source: Reference 24

[a]Value in parenthesis is the number of observations for the quarterly average.

TABLE 3-21. AMBIENT CONCENTRATIONS OF PaH AT FLORENCE, ALABAMA, DECEMBER 23, 1981 - MARCH 22, 1983 (ng/m^3) (PEDCo GC/MS METHOD)

Date	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a) anthracene	Chrysene/ Triphenylene	Benzo(e) pyrene[a]	Benzo(a) pyrene	Perylene	Benzo(k) fluoranthene[a]	Total
Residential											
12/27	0.08	0.06	0.25	0.27	1.4	1.0	0.75	0.15	-[a]	3.7	7.6
12/30	2.2	0.13	0.45	0.42	1.2	1.0	3.5	2.6	-	10.8	20.3
12/31	0.10	-	0.38	0.37	1.2	1.7	1.4	0.67	0.35	7.4	13.5
1/3	0.04	0.03	0.26	0.29	0.28	0.81	18.1	0.41	0.29	52.7	73.2
1/7	-	-	0.70	0.66	0.37	0.71	0.27	0.32	-		3.0
1/17	-	-	0.50	0.47	0.75	3.0	1.7	0.80	0.20		7.5
1/19	0.10	0.08	0.60	0.64	0.34	0.78	3.4	2.5	0.23	7.2	15.9
1/26	0.49	-	1.2	1.3	1.1	2.0	0.76	0.76	0.14		7.8
1/27	-	-	0.78	0.89	-	2.5	0.84	0.69	0.16		5.8
2/2	0.02	-	0.31	0.30	0.28	0.77	0.52	0.51	0.12		2.8
2/4	0.12	-	0.25	0.23	-	0.18	-	-	-		0.78
2/13	0.18	-	3.5	4.2	5.5	8.3	3.8	5.4	0.56		31.4
2/17	0.06	0.06	0.12	0.12	0.04	0.15		-	-	-	0.56
2/18	0.05	-	0.17	0.18	0.16	0.51	1.7	0.20	-	5.6	8.5
3/1	0.04	-	0.19	0.18	0.20	0.46	1.3	1.0	0.04	8.2	11.6
3/6	0.05	-	0.17	0.17	-	0.17	-	-	-		0.56
3/10	1.1	0.83	1.6	1.7	1.2	2.5	1.5	1.1	1.0		12.6
Rural											
1/3	-	-	0.09	0.09	0.10	0.23	0.04	-	-		0.53
1/7	0.12	-	0.52	0.49	0.61	0.44	-	-	-	-	2.2
1/19	-	-	0.08	0.10	-	0.12	-	-	-		0.30
2/2	1.14	-	0.48	0.44	0.27	0.43	0.31	-	-		2.1
2/4	-	-	0.30	0.22	0.07	0.21	0.03	-	-		0.83
2/10	0.09	0.04	0.39	0.37	0.47	2.0	2.8	0.36	-	9.5	16.1
2/18	0.05	-	0.16	0.14	-	0.21	0.30	-	-	1.5	2.4
3/18	0.09	-	0.13	0.14	-	-	-	-	-		0.36

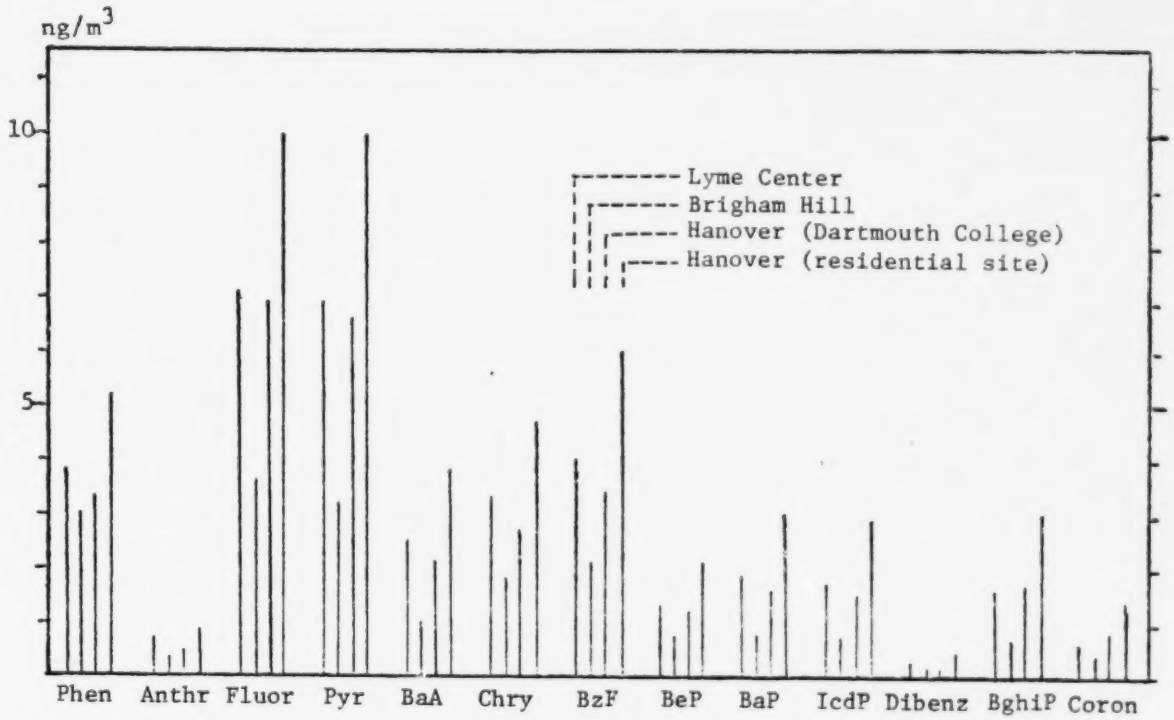
[a]Some values appear high and are being reanalyzed. A dash indicates the value was below detectable limits while a blank indicates that the compound was not analyzed for.

3.2.9 Soderberg et al., 1983

Soderberg et al. collected standard high-volume filter samples of ambient air particulates during the winter of 1981-82 in a semi-rural village (Lyme Center, NH), a rural area (Brigham Hill, VT), and a residential neighborhood and college campus in a small town (Hanover, NH). Three of these sites (Lyme Center, Brigham Hill, and residential Hanover) were the subjects of a similar sampling campaign during the winter of 1979-80 (reported in Section 3.2.4). Samples were collected continuously over 24-hr and 48-hr periods for two weeks.

Extensive development work on extraction and clean-up schemes resulted in a reproducible procedure based on extraction of the filters with cyclohexane using ultrasonic agitation, chromatography of silica gel, and extraction of the PAH fraction into dimethyl sulfide. Concentrations of 13 PAHs were determined by high performance liquid chromatography and by gas chromatography using both flame ionization and mass spectrometric detection.

Measurements of PAH concentrations in ambient air particulates at the four sites were reported in graph form only, which is reproduced as Figure 3-1. Concentrations of the 13 PAH compounds generally followed the same pattern at the four sites and range from less than 1 ng/m^3 to approximately 10 ng/m^3. Brigham Hill exhibits the lowest concentrations, followed by Hanover (Dartmouth College), Lyme Center, and Hanover (residential site). Average concentrations of B(ghi)P and coronene at the Dartmouth College site were slightly higher than concentrations found in Lyme Center, which are the only exceptions to this overall pattern. Previous studies have reported that the presence of B(ghi)P and coronene correlates with auto emissions.



Phen = phenanthrene, Anthr = anthracene, Fluor = fluoranthene,
Pyr = pyrene, BaA = benz(a)anthracene, Chry = chrysene,
BzF = benzfluoranthenes, BeP = benz(e)pyrene, BaP = benz(a)pyrene,
IcdP = indeno (1,2,3-cd)pyrene, Dibenz = dibenzanthracenes,
BghiP = benzo(g,h,i)perylene, Coron = coronene

Figure 3-1. Average PAH Profiles: Lyme Center, Brigham Hill, Hanover (Dartmouth College), Hanover (Residential Site). January 15-31, 1982.

The authors reported the following observations from the data collected in this study and from an analysis of PAH analytical techniques:

1. The authors compared ultrasonic and Soxhlet extractions of identical samples with three solvents: cyclohexane, toluene/ethanol, and methylene chloride (see Table 3-22). They also conducted a more extensive comparison of solvents for ultrasonic extractions (see Table 3-23). None of these extractions gave complete recoveries of spiked PAH compounds (see Table 3-24). Therefore, the measured levels of ambient PAHs incorporated in air particulates must be considered lower limits for the actual PAH content.

2. Cyclohexane, toluene/ethanol, and methylene chloride are comparable solvents for the extraction of PAHs.

3. Ultrasonic and Soxhlet extraction are roughly equivalent techniques.

4. Resolution using fused-silica capillary-column gas chromatography was excellent, generally making the less convenient high pressure liquid chromatography method unnecessary, except when resolution of triphenylene-chrysene and of the three benzfluoranthenes was desired. Both techniques are reproducible within relative standard deviations of about 5 percent and give similar quantitative results (see Table 3-25).

5. The similarity of the patterns of the relative concentrations of the 13 PAHs was not anticipated. The proximity of the Hanover sites to substantial amounts of automobile and truck traffic and to domestic and institutional oil burning was expected to produce a different mix of PAH

TABLE 3-22. COMPARISON OF SOXHLET AND ULTRASONIC EXTRACTION BY THREE DIFFERENT SOLVENTS**

Solvent / Technique*	Cyclohexane		Tol/ethanol		CH_2Cl_2	
	1	2	1	2	1	2
Phenanthrene	1.00	0.81	1.06	0.79	0.77	1.15
Anthracene	1.00	0.81	1.32	1.24	0.67	1.09
Fluoranthene	1.00	0.80	1.01	0.78	0.84	1.07
Pyrene	1.00	0.84	1.00	0.80	0.82	1.14
Benz(a)anthracene	1.00	0.99	0.97	1.04	0.79	1.08
Chrysene	1.00	0.80	0.83	0.80	0.77	1.03
Benzfluoranthenes	1.00	0.87	1.05	0.94	0.79	1.06
Benz(e)pyrene	1.00	0.85	0.94	0.96	0.82	1.00
Benz(a)pyrene	1.00	0.83	0.98	0.91	0.79	1.06
Indeno(c,d)pyrene	1.00	0.87	0.95	0.99	0.79	0.90
Dibenz(a,h)anthracene	1.00	0.74	0.70	0.94	0.60	0.60
Benzo(g,h,i)perylene	1.00	0.89	1.12	1.01	0.86	1.01

*1 = Ultrasonication
2 = Soxhlet

**Eighteen identical composite ambient air filter samples were used, with each extraction carried out in triplicate. Each extract was analyzed three times by GC/FID. Results are reported as the ratio to ultrasonic extraction with cyclohexane. Relative standard deviations were less than eight percent.

TABLE 3-23. COMPARISON OF SOLVENTS FOR FILTER EXTRACTION BY ULTRASONIC AGITATION*

PAH	C	T-E	MC	B	CS_2	DMSO
Phenanthrene	1.00	1.06	0.77	0.99	1.04	1.02
Anthracene	1.00	1.32	0.67	1.03	1.00	1.03
Methylphenanthrene	1.00			1.25	1.20	1.09
Fluoranthene	1.00	1.01	0.84	1.11	1.27	1.03
Pyrene	1.00	1.00	0.82	1.22	1.31	1.06
Benz(a)anthracene	1.00	0.97	0.79	1.28	1.19	0.92
Chrysene	1.00	0.83	0.77	1.18	1.27	0.97
Benzfluoranthenes	1.00	1.05	0.79	1.25	1.28	0.98
Benz(e)pyrene	1.00	0.94	0.84	1.31	1.30	1.05
Benz(a)pyrene	1.00	0.98	0.79	1.21	1.31	1.04
Indeno(c,d)pyrene	1.00	0.95	0.79	1.16	1.19	1.05
Dibenz(a,h)anthracene	1.00	0.70	0.60	0.70	0.73	0.63
Benzo(g,h,i)perylene	1.00	1.12	0.86	1.23	1.25	1.07
Coronene	1.00			1.26	0.93	1.04

*Eighteen identical composite filters were prepared, and three were used with each solvent. Results are reported relative to cyclohexane. The relative standard deviation was less than 5 percent.

C = cyclohexane
B = benzene
T-E = toluene/ethanol
MC = methylene chloride
DMSO = dimethyl sulfoxide
CS_2 = carbon disulfide

TABLE 3-24. RECOVERY OF POM USING PREFERRED PURIFICATION SCHEME*

PAH	Percent Recovery		
	1	2	3
Phenanthrene	77.4	55.5	43.0
Anthracene	62.7	50.4	55.0
Methylphenanthrene	66.9	50.8	48.7
Fluoranthene	80.7	73.7	70.2
Pyrene	79.4	70.4	67.1
Benz(a)anthracene	82.6	93.5	95.3
Chrysene	97.0	90.7	87.0
Benz(j)fluoranthene	89.7	95.3	83.9
Benz(e)pyrene	94.2	93.2	85.7
Benz(a)pyrene	91.3	97.2	85.7
Indeno(c,d)pyrene	80.5	98.0	87.1
Dibenz(a,h)anthracene	90.6	96.7	92.3
Benzo(g,h,i)perylene	83.7	91.9	80.2
Coronene	94.7	99.0	88.7

*GC/MS analysis using chrysene-d 12 internal standard; 1 = recovery from simulated filter extract; 2 = recovery from spiked blank filter; 3 = recovery from spiked filter containing pre-extracted particulates.

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TABLE 3-25. COMPARISON OF GC AND HPLC ANALYSIS OF POM*

PAH	Amount Found (ng) + RSD (%)**			
	GS/MS		HPLC	
Phenanthrene	580	6.2	654	10
Anthracene	44	16	62	4.8
Fluoranthene	2820	9.5	3060	5.7
Pyrene	2460	3.0	2660	5.0
Benz(a)anthracene	2730	1.8	3180	4.0
Triphenylene			1090	5.8
Chrysene			4340	4.2
Chrysene/triphenylene	5520	4.0	5430	4.2
Benz(j)fluoranthene			2560	1.3
Benz(b)fluoranthene			4550	4.6
Benz(k)fluoranthene			1870	0.75
Benzfluoranthenes	8800	4.1	8980	2.4
Benz(e)pyrene	3230	4.5	3450	3.2
Benz(a)pyrene	3030	3.1	3270	7.2
Indeno(1,2,3-c,d)pyrene	3250	5.1	2830	7.9
Dibenz(a,h)anthracene	480	4.8	1620	12
Benzo(g,h,i)perylene	3500	5.5	3560	7.4

*Average of three identical composite filters. Finnigan 4000 GC/MS; Perkin Elmer series III HPLC.

**Relative standard deviation, N = 3.

compounds at each site. The authors conclude from these data, and "very low" summertime PAH levels observed at the sites (unreferenced), that the dominant source of wintertime PAHs at all four sites is wood burning.

6. The concentrations of BaP are "substantially" higher than those reported for rural New Hampshire and Vermont in 1970 (25).

7. Levoglucosan (1,6-anhydro-B-ϕ-glucopyranose) is a potentially useful qualitative and semiquantitative tracer for wood smoke. It does not arise from the burning of fossil fuels.

8. The authors note that more recent sampling efforts (1982-1983) show that losses of the more volatile low molecular weight PAHs from the particulate mass are likely to be substantial, especially on warmer days.

Sampling and analysis for ambient concentrations of PAH compounds at these sites continues. During 1982-1983, the authors are studying the correlation between concentrations of BaP and levoglucosan in ambient air particulates.

3.3 Trends

BaP concentrations have definitely been decreasing in many areas during the last 15 years. Factors associated with this decline include enforcement of the provisions of the state implementation plans governing particulate emissions from coke ovens, utilities, automobiles, and open burning; a general economic slowdown; and decreased utility coal combustion.

This trend may be reversed in some areas through increases in both residential and industrial wood burning, combustion of refuse-derived fuel, increases in vehicular traffic, and changing vehicle fuel use patterns (increasing use of diesel in autos). The reemergence of coal combustion would

also affect POM concentrations. The substantial increase in BaP concentrations from 1970 to 1981-82 reported by Soderberg et al. (1983) for rural New Hampshire and Vermont is attributed largely to the revival of residential wood burning. In New York City, Daisey, Hershman, and Kneip (1982) found that although TSP concentrations declined significantly from 1968 to 1978, total organic emissions showed little change. Particulate organic matter, as a percentage of TSP, increased substantially in 1977 and 1978 as compared to the earlier years (1968-69). However, these comparisons are based on limited data obtained using different sample extraction procedures. Therefore, the measurements may not be directly comparable.

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4.0 SAMPLING AND ANALYTICAL CONSIDERATIONS

The sampling and analytical methodologies employed in the determination of ambient levels of POM may in certain cases have a significant impact on the reported data. The RTI report (1) evaluated POM sampling and analytical methodologies and concluded that historical data should be viewed as semi-quantitative at best. More recent research indicates that the uncertainty with respect to the accuracy of POM sampling and analytical techniques has not been resolved (2, 3, 4). Caution should therefore be exercised in the interpretation, comparison, and use of POM ambient concentration data.

4.1 Sampling Methodologies

The accuracy of sample collection is a particularly significant concern when ambient concentrations are at trace levels, such as with POM. Measured levels of POM can be affected by the precision of the collection technique, incomplete collection, the location of the sampling equipment, and the frequency of sampling.

4.1.1 Collection Technique Precision

Sampling for POM in the ambient atmosphere has relied heavily on the collection of suspended particulates. The mainstay of the National Air Surveillance Network (NASN) program and many individual research projects has been the high volume sampler. Several factors are critical to the accuracy of the high volume sampler, the most important of which is the consistency of the flow rate. The RTI report (1) estimates that filter clogging can cause as much as 50 percent deviation from the true particulate average by reducing the flow rate. The report concludes, however, that the high volume sampler has repeatedly proven its reliability when operated according to standard methods.

4.1.2 Incomplete Collection

The actual applicability of filter samplers in general to POM sampling is subject to debate. The RTI report (1) found that losses of POM might occur as a result of desorption from the filter surface, failure to collect vapor-phase POM, and chemical rearrangements of POM on the filter surface. The report concludes that "since the loss of vapor phase POM appears to be negligible when sampling ambient air at high velocities and at ambient temperatures, the most likely explanation for the losses appears to be via chemical rearrangement." Hornig et al. (4) have suggested using Teflon coated filters to minimize degradation on the filter and handling samples in rooms equipped with yellow fluorescent light to minimize chances of photooxidation.

Although the RTI report (1) found no conclusive evidence of the presence of POM in the vapor phase in the ambient atmosphere, Handa et al. (2) conclude that some PAHs remain in the vapor phase, particularly in summer. They were able to capture from 4.7 percent to 71.3 percent more PAH using traps cooled by liquid nitrogen than with a high volume air sampler. Manning et al. (10) also report the existence of vapor-phase PAH. These data contradict the findings of Miguel and Friedlander (5), as described in the RTI report, who did not detect BaP in the vapor phase using a high volume glass fiber filter backed by two cold traps in series. Handa et al. suggest, however, that volatilization of PAHs collected on the filter could also be a cause for the lower recovery in high volume air samplers. They do not present data to prove the existence of vapor phase PAH.

Katz and Chan (3) show that the soluble organic fraction and the concentrations of pentacyclic and hexacyclic PAHs in samples collected at flow rates of about 0.57 m^3/min. by a cascade impactor are consistently higher than corresponding values in samples collected at higher flow rates by high-volume filtration. They ascribe the differences, which ranged from negligible to more than 500 percent for individual PAHs, to losses by volatilization or sublimation.

Measured levels of POM may also underestimate ambient concentrations through inefficient collection of fine particulates. There are reports that more than 50 percent of some POMs may be on particles too small to be collected on glass fiber filters (4). Katz and Chan (3) found from 19.4 to 46.7 percent of some PAHs in the particle size fraction < 1.1 μm. They conclude that particles greater than 10 μm contribute significantly to the aerosol mass but add little to the concentration of PAHs.

4.1.3 Location of the Sampling Point

The RTI report (1) cautions that the location of the sampling point is crucial in ambient sampling. An analysis of the results of sampling by Greenberg and Darack (6) illustrate the danger of considering a sample taken from a single point as representative of an area. Composite data indicated that PAH concentrations in Newark, New Jersey were double those in Elizabeth and Camden. However, the authors note that daily sample analyses indicated that the high apparent concentration in the Newark composite reflected a very high level of PAH on one day and, without this event, the Newark site is only slightly higher in PAH concentrations than the other two urban locations. They suggest that the singularity resulted from a "local combustion source."

4.1.4 Sample Frequency

The RTI report (1) also discusses the importance of the frequency of sample collection. Samples should be taken at a frequency sufficient to determine the influence of meteorology, the effect of topography, and the variations in the productivity of the emissions sources. Daily samples yield the most accurate information. The accuracy decreases as the time interval between samples is increased.

4.2 Analytical Techniques

Analytical techniques involved in the quantification of POM have evolved from simple fluorescent techniques to computerized gas chromatograpy/mass spectrometry (GC/MS). The main advances in analysis have involved improved resolution, thus increasing the number of identifiable compounds.

The RTI report (1) reviews a variety of analytical techniques currently being used to determine POM concentrations. The report indicates that:

1. Hundreds of POM compounds may be present in environmental samples. The number of POM compounds reported for a given sample may vary substantially, thus reflecting the limitations of the specific analytical technique used.

2. Agreement between POM concentrations obtained using different analytical techniques can be expected to be no better than an order of magnitude.

3. Quantitative data for POM concentrations will generally be less than actual concentrations.

Basically the hundreds of methods for POM analysis share a common format of six steps: (1) extraction, (2) concentration, (3) enrichment, (4) resolution, (5) identification, and (6) quantification. There is, however, no standard technique for POM analysis and significant variations in methods exist for each of these six steps (1).

The effectiveness of different analytical methods is difficult to assess. Although agreement within a factor of two is common for intralaboratory comparisons of methods for POM analysis, test mixtures containing POM standards do not approach the complexity of environmental samples (1).

Several researchers have suggested methods to improve POM analytical techniques. Hornig et al. (4) switched to sample extraction by sonification instead of Soxhlet extraction in order to reduce the time and severity of that step. They also adopted a solvent extraction technique to clean up the samples before analysis by high pressure liquid chromatography or GC/MS. In a later study (7), however, these researchers determined that ultrasonic and Soxhlet extraction are roughly equivalent techniques, although neither gives complete recovery of spiked PAH samples. They also found that cyclohexane, toluene/ethanol, and methylene chloride are comparable solvents for the extraction of PAHs. In addition, they decided that resolution using fused-silica capillary-column gas chromatography was excellent, generally making the less convenient high pressure liquid chromatography method unnecessary, except for a few compounds.

The comparability of results of analyses for specific POM compounds as representative of total POM is also difficult to assess. Most researchers analyze for specific POM compounds, typically BaP and other PAH. No two researchers cited in this report analyzed for the same array of compounds. Daisey, Hershman, and Kneip (8) and Harkov, Daisey, and Lioy (9) analyzed for total POM (defined as particulate organic matter rather than polycyclic organic matter) using a three-solvent sequential Soxhlet extraction. Their data, however, overestimate the concentration of polycyclic organic matter in ambient air because particulate organic matter includes more compounds than does polycyclic organic matter.

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